

Open-shell restricted Hartree–Fock perturbation theory: Some considerations and comparisons

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A comparative study is presented of the various recently developed open-shell perturbation theories that are based on a restricted Hartree–Fock reference wave function. Included in this study are issues concerning spin contamination, implementational considerations, and numerical comparisons at the second-order of perturbation theory for equilibrium geometries, vibrational frequencies, and singlet–triplet energy differences. Based on all of these considerations, it is concluded that the z -averaged perturbation theory (ZAPT) method is to be preferred over the other recently devised spin–orbital perturbation theories, while the spin-free OPT2 method possesses some advantages and disadvantages relative to the ZAPT method. In particular, it is shown that OPT2 energies are not invariant to rotations among singly-occupied degenerate molecular orbitals.

I. INTRODUCTION

There has been considerable interest recently in formulating an open-shell perturbation theory that is based on a restricted Hartree–Fock (RHF) reference wave function.^{1–6} There has also been much interest in developing an efficient and accurate multireference perturbation theory (e.g., see Refs. 7–13), but we shall limit our discussion here to single-reference based approaches. The methods that have been developed thus far may be placed into two classes, those that use a configuration state-function (CSF) basis^{1,5} (i.e., S^2 eigenfunctions), and those that use a spin–orbital determinant basis.^{2–4,6} Approaches in the first group include the OPT1 and OPT2 methods of Murray and Davidson,⁵ as well as the method proposed by Hubac and Carsky.¹ The RMP,³ ROMP,² and ZAPT (Ref. 6) methods comprise the second group (note that the ROHF-MBPT method of Bartlett and co-workers⁴ gives identical energies to the RMP method). However, based on the evidence available thus far,^{2–6,14–17} the success or nonsuccess of a particular perturbation theory is not determined by the choice of n -particle basis, but rather is determined by the choice of the diagonal matrix elements that make up the denominators. In other words, it has been shown empirically that a given perturbation series typically converges more rapidly the larger the denominators (with the proviso, of course, that the denominators are still physically meaningful and not simply large numbers).¹⁴ Larger denominators certainly require that the second-order correlation energy be smaller in magnitude, but these perturbation series also show few if any oscillations (for example, see Refs. 2,3,15,18). Based on these analyses and also on some numerical tests, it has been asserted^{12,15} that the perturbation

series for the OPT1 method and also the method of Hubac and Carsky will not converge as rapidly as the perturbation series for the other methods (i.e., OPT2, RMP, ROMP, and ZAPT).

As well as convergence of the perturbation series, there are several other aspects to consider when evaluating RHF open-shell perturbation theories. As mentioned above, some of the methods (OPT1 and OPT2) possess n th-order wave functions that are eigenfunctions of S^2 , which is important if spin-dependent properties are to be investigated. Several of the methods (OPT1, OPT2, and ZAPT) require that the spatial parts of α and β spin-orbitals be identical, which has obvious computational advantages. Finally, some of the recently developed RHF open-shell perturbation theories (RMP and ROMP) possess different α and β spatial orbitals, as well as having n th-order wave functions that are not S^2 eigenfunctions, but their perturbation series have been shown^{2,3,15} to converge much more rapidly than conventional unrestricted Møller–Plesset (MP) perturbation theory. It should also be mentioned that spin projection of the unrestricted MP series has been investigated,¹⁹ but because these methods are limited in the number of spin contaminants projected out, the perturbation energies lose the property of size-extensivity (as discussed by Schlegel¹⁹). Size-extensivity has been shown to be an important property over the last several years (especially when treating a large number of electrons), and therefore these partially projected schemes do not appear promising.

The determinant based methods, ZAPT, ROMP, and RMP, are all quite similar in their formulation. RHF open-shell molecular orbitals are employed and H_0 is defined from diagonal elements of the spin–orbital Fock operator. How-

ever, the wave functions in ZAPT are S_x eigenfunctions whereas those in RMP and ROMP theory are S_z eigenfunctions. RMP and ROMP differ only in their choice of canonicalization procedure for the molecular orbitals.

The purpose of the present investigation is to evaluate the different RHF open-shell perturbation theories in three areas. (1) The degree of spin contamination, or in other words, how does the spin contamination appear and at what order are the energy and perturbed wave function affected; (2) the computational cost of each method and how this compares to the computational cost of a closed-shell RHF MP calculation, as well as other implementation considerations; (3) the quality of numerical results obtained from each method at second-order, and how they compare to experiment when using large one-particle basis sets. These three aspects are discussed in the following three sections, respectively, while our conclusions are given in the final section.

II. SPIN CONTAMINATION

The spin properties of the OPT1 and OPT2 methods have been discussed in detail previously.⁵ Because H_0 is independent of spin in these theories, the n th-order perturbed wave functions Ψ_n will be S^2 eigenfunctions, and there is no spin contamination. For all of the determinant based methods (i.e., RMP, ROMP, and ZAPT), H_0 is spin dependent and does not commute with S^2 . Thus, all of these methods will possess some degree of spin contamination. It has been noted (e.g., see Refs. 3,4,6) that since the reference function is an S^2 eigenfunction, the perturbation series is automatically spin projected. Thus the projected n th-order energy \tilde{E}_n and the unprojected n th-order energy E_n are the same,

$$\begin{aligned}\tilde{E}_n &\equiv \langle \Psi_0 | V O | \Psi_{n-1} \rangle \\ &= \langle \Psi_0 | (H - H_0) O | \Psi_{n-1} \rangle = \langle \Psi_0 | (H - E_0) O | \Psi_{n-1} \rangle \\ &= \langle \Psi_0 | O (H - E_0) | \Psi_{n-1} \rangle = \langle \Psi_0 | V | \Psi_{n-1} \rangle = E_n.\end{aligned}\quad (1)$$

In the above equations, we have used the fact that O (the projector which enforces spin symmetry) and H commute, and the fact that Ψ_0 is a spin and H_0 eigenfunction. However, as discussed by Murray *et al.*,^{14,15} the above proof shows only that there will be no direct contribution from a spin contaminant. In fact, the first and higher-order perturbed wave functions are contaminated, so that there will be an indirect contribution from spin contamination to E_3 and higher-order energies. Interestingly, E_2 will not contain any contamination under these conditions. This is discussed in more detail later.

First, we examine which parts of H_0 introduce spin contamination in the various theories. Employing the language of second quantization, H_0 for ZAPT may be written in the form

$$H_0 = \epsilon_i E_{ii} + \epsilon_a E_{aa} + \frac{1}{2}(\epsilon_s^+ + \epsilon_s^-) E_{ss} + \frac{1}{2}(\epsilon_s^+ - \epsilon_s^-) \dot{E}_{ss}, \quad (2)$$

where indices i , a , and s refer to doubly occupied, virtual, and singly occupied spatial orbitals, respectively, and sum-

mation over these indices is implied. The eigenvalues ϵ are defined as the appropriate diagonal elements of the ZAPT canonicalized spin-orbital Fock matrix,⁶

$$\begin{aligned}\epsilon_i &= F_{i\alpha}^{i\alpha} = F_{i\beta}^{i\beta}, & \epsilon_a &= F_{a\alpha}^{a\alpha} = F_{a\beta}^{a\beta}, \\ \epsilon_s^+ &= F_{s\sigma^+}^{s\sigma^+}, & \epsilon_s^- &= F_{s\sigma^-}^{s\sigma^-}.\end{aligned}\quad (3)$$

E_{pq} are the standard unitary group generators (p and q refer to any spatial molecular orbital)

$$E_{pq} = (p\alpha)^\dagger (q\alpha) + (p\beta)^\dagger (q\beta) \quad (4)$$

and \dot{E}_{pq} are spin-flip analogs of the $U(n)$ generators defined previously²⁰

$$\dot{E}_{pq} = (p\alpha)^\dagger (q\beta) + (p\beta)^\dagger (q\alpha). \quad (5)$$

Also, recall that the σ^+ and σ^- spin functions were defined²¹ according to

$$\sigma^+ = \frac{1}{\sqrt{2}} (\alpha + \beta), \quad (6)$$

$$\sigma^- = \frac{1}{\sqrt{2}} (\alpha - \beta). \quad (7)$$

It is well known that the E_{pq} generators commute with S^2 , however, it was shown²⁰ that the spin-flip analogs \dot{E}_{pq} do not commute with S^2 . Thus, it is evident that the ZAPT H_0 does not commute with S^2 and that only the last term of H_0 will give rise to spin contamination. Note that the OPT1 H_0 is obtained by deleting the last term in Eq. (2). It is also interesting to note here a significant difference between ZAPT and the RMP and ROMP methods. Due to the fact that the $\{f_{i\alpha}^{i\alpha}, f_{i\beta}^{i\beta}\}$ and $\{f_{a\alpha}^{a\alpha}, f_{a\beta}^{a\beta}\}$ pairs of Fock matrix elements are different in RMP and ROMP theory, their H_0 will contain significantly more terms, relative to ZAPT, that do not commute with S^2 . For example, the RMP or ROMP H_0 may be written as

$$H_0 = f_i^+ E_{ii} + f_a^+ E_{aa} + f_s^+ E_{ss} + f_i^- E_{ii} + f_a^- E_{aa} + f_s^- E_{ss}, \quad (8)$$

where

$$f_p^+ = \frac{1}{2}(f_{p\alpha}^{p\alpha} + f_{p\beta}^{p\beta}), \quad (9)$$

$$f_p^- = \frac{1}{2}(f_{p\alpha}^{p\alpha} - f_{p\beta}^{p\beta}), \quad (10)$$

$$E_{pq}^- = (p\alpha)^\dagger (q\alpha) - (p\beta)^\dagger (q\beta), \quad (11)$$

where $\{f_{p\alpha}^{p\alpha}, f_{p\beta}^{p\beta}\}$ are the appropriate spin-orbital Fock matrix elements. Alternatively, the RMP or ROMP H_0 may be written in z -averaged form (see Ref. 20),

$$H_0 = f_i^+ E_{ii} + f_a^+ E_{aa} + f_s^+ E_{ss} + f_i^- \dot{E}_{ii} + f_a^- \dot{E}_{aa} + f_s^- \dot{E}_{ss}. \quad (12)$$

Because S^2 does not commute with either \dot{E}_{pq} or E_{pq}^- , spin contamination arises from all of the molecular orbitals, not just from the singly occupied orbitals as is the case for ZAPT. Of course, this in itself does not prove that spin con-

tamination in the RMP and ROMP methods will be numerically larger than for ZAPT, but it is suggestive.

For completeness, the OPT2 choice for H_0 is given by

$$H_0 = \epsilon_i E_{ii} + \epsilon_a E_{aa} + \frac{1}{2}(\epsilon_s^+ + \epsilon_s^-) E_{ss} - \frac{1}{2}(\epsilon_s^+ - \epsilon_s^-) E_{ss}(E_{ss} - 2). \quad (13)$$

Although this H_0 has no spin-symmetry breaking parts, and similar to ZAPT allows two eigenvalues to be associated with a singly occupied orbital, these advantages have been achieved at the expense of introducing a more complicated two-particle H_0 .

Next, we examine how spin contamination enters the first-order wave function as a result of using a spin dependent H_0 . The general expression for the first-order wave function is

$$\Psi_1 = R^{-1} V \Psi_0, \quad (14)$$

where

$$R^{-1} = P(E_0 - H_0)^{-1} P, \quad (15)$$

$$V = (H - H_0), \quad (16)$$

$$P = 1 - |\Psi_0\rangle\langle\Psi_0|. \quad (17)$$

The operator R^{-1} is the resolvent, and is a pseudoinverse. V is the perturbation, and P is the projector onto the orthogonal complement of Ψ_0 , which defines the domain of the resolvent. Examination of the commutator $[S^2, R^{-1}V]$ gives

$$\begin{aligned} [S^2, R^{-1}V] &= R^{-1}[S^2, V] + [S^2, R^{-1}]V \\ &= -R^{-1}[S^2, H_0] - R^{-1}[S^2, R]R^{-1}V \\ &= -R^{-1}[S^2, H_0] + R^{-1}[S^2, H_0]R^{-1}V \\ &= R^{-1}[S^2, H_0](R^{-1}V - 1), \end{aligned} \quad (18)$$

where we have used the fact that S^2 commutes with H and P . We have also used the identities

$$\begin{aligned} [A, BC] &= B[A, C] + [A, B]C, \\ [A, B^{-1}] &= -B^{-1}[A, B]B^{-1}. \end{aligned} \quad (19)$$

The latter identity may be used even with a pseudoinverse, as here, provided that A commutes with the projector defining the pseudoinverse domain. Using the above results, it is easily shown that

$$S^2\Psi_1 = s(s+1)\Psi_1 + R^{-1}[S^2, H_0]\Psi_1. \quad (20)$$

This shows that the first-order wave function is contaminated, in general, because S^2 does not commute with H_0 , and that the contamination is proportional to the product of the resolvent and the commutator of S^2 and H_0 . This is a general expression valid for any spin-orbital perturbation theory which is subject to contamination. Clearly, the contamination is of the same order in V as in Ψ_1 , as noted by other authors.^{23,24} However, the presence of the energy denominator R^{-1} indicates that numerically, the contamination may be more appropriately grouped in the next higher order, because, as noted by Murray and Davidson,¹⁴ the energy denominator plays a more important role than V in determining the size of the perturbation correction. Of course, this is en-

tirely dependent on the size of $[S^2, H_0]$. As noted before, there will be many more H_0 terms in RMP and ROMP theory (relative to ZAPT) that do not commute with S^2 . Therefore, except in situations of fortuitous error cancellation, the magnitude of spin contamination will be larger for these methods than for ZAPT.

Finally, we examine how spin contamination comes about in the perturbed energy expressions. At second-order,

$$E_2 = \langle\Psi_0|VR^{-1}V|\Psi_0\rangle = \langle\Psi_0|H|i\rangle\langle i|R^{-1}|i\rangle\langle i|H|\Psi_0\rangle, \quad (21)$$

where we have inserted a resolution of the identity as a sum over determinant eigenfunctions of H_0 , used the fact that R^{-1} is diagonal in this basis, and used the fact that $\langle\Psi_0|V|i\rangle = \langle\Psi_0|H|i\rangle$ (because the sum over i never includes Ψ_0). Since Ψ_0 is an S^2 eigenfunction and H does not break spin symmetry, there can be only spin pure contributions from the sum over i . Thus E_2 contains no contributions from spin contaminants, as noted previously. (This is not inconsistent with the fact that Ψ_1 is contaminated.) At higher order, this is no longer the case. For example, at third-order one contribution will be (see Ref. 24)

$$\langle\Psi_0|V|i\rangle\langle i|R^{-1}|i\rangle\langle i|V|j\rangle\langle j|R^{-1}|j\rangle\langle j|V|\Psi_0\rangle. \quad (22)$$

First note that $\langle i|V|j\rangle = \langle i|H|j\rangle$ for the off-diagonal elements (i.e., $i \neq j$). Therefore, in the determinant basis spin contamination is not introduced from off-diagonal elements of V . This is simply a generalization of the situation at second-order. Clearly, the majority of matrix elements will be off-diagonal. Second, note that contamination must also arise from the resolvent R^{-1} . Indeed, this is clearly where the contamination arises in the first-order wave function (i.e., if S^2 commutes with R^{-1} , then Ψ_1 is an eigenfunction of S^2). Another way to view the spin contamination (without loss of generality) is by the use of a CSF basis. In this case the resolvent has off-diagonal matrix elements that connect states of different spin. Thus, in the case of the third-order contribution above, if we regard the intermediate summations to be over CSFs rather than determinants (taking into account that the resolvent is no longer diagonal in this basis), one sees that contamination may arise only over the central matrix element of V .

In view of this analysis, it is evident that in a determinant basis spin contamination for ZAPT can arise only from diagonal matrix elements involving determinants which differ from the reference determinant Ψ_0 in their singly occupied (spin) orbitals. This is because the only term in H_0 for ZAPT which breaks spin symmetry is the one involving those orbitals. Again, the majority of matrix elements in ZAPT are unaffected by contamination. This is in contrast to methods such as RMP or ROMP, where all matrix elements for which spin contamination is possible will contribute some contamination to a greater or lesser extent. It is thus apparent that the ZAPT H_0 represents a good compromise between the theoretical desire to minimize spin contamination and retain a simple H_0 , and the practical considerations of efficiency and good series convergence (based on the physically appealing model of having two types of singly occupied orbitals distinguished only by their eigenvalue).

III. IMPLEMENTATIONAL CONSIDERATIONS

Ignoring the integral transformation step, the computational cost of the RMP and ROMP methods is clearly the same as standard unrestricted MP theory, due to the different α and β spatial orbitals. Thus, for the evaluation of E_2 , the computational cost of RMP and ROMP will be about three times that of an analogous closed-shell MP2 calculation, and this factor will become larger for higher-order energies. The computational cost for the transformation step is ignored, since this is a fixed cost and therefore the computational effort of the higher-order energies will be significantly greater than that of the transformation step. We do note, however, that Knowles *et al.*³ showed that the transformation step for the RMP and ROMP methods may be written in a form in which the computational cost is less than that for the unrestricted MP case. The computational cost of the OPT1, OPT2, and ZAPT methods is more complicated, and we begin by examining the second-order energy expressions. We note first that the molecular orbital canonicalization schemes defined for OPT1, OPT2, and ZAPT are all the same, and

therefore the molecular orbital integrals are identical for all three methods. In the following equations i and j shall refer to doubly occupied spatial molecular orbitals in the reference function, a and b refer to unoccupied molecular orbitals, s and t refer to singly occupied orbitals, and m, n, p , and q refer to any spatial molecular orbitals. Also, v_{mn}^{pq} represent the $(mp|nq)$ two-electron integral in Mulliken notation. It is necessary to define the different "orbital energies" that are used. For ZAPT the diagonal elements of the symmetric spin orbital Fock matrix are $\epsilon_i, \epsilon_a, \epsilon_s^+$, and ϵ_s^- , as defined in Eqs. (3). The "orbital energies" for the doubly occupied orbitals i and the unoccupied orbitals a for OPT1 and OPT2 are the same as those in ZAPT, but the singly occupied "orbital energies" are different. Hence we define f_s as

$$f_s = \frac{1}{2} (\epsilon_s^+ + \epsilon_s^-). \quad (23)$$

Using these definitions, the ZAPT, OPT1, and OPT2 second-order energies may be written as

$$E_2^{\text{ZAPT}} = \frac{1}{2} \sum_{ia} \frac{K_i^a K_i^a}{\epsilon_i - \epsilon_a} + \sum_{sjbt} \frac{v_{sj}^{bt} v_{sj}^{bt}}{\epsilon_s^+ + \epsilon_j - \epsilon_b - \epsilon_t^-} + \sum_{ijab} \frac{v_{ij}^{ab} (2v_{ij}^{ab} - v_{ji}^{ab})}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} + \sum_{sjab} \frac{v_{sj}^{ab} (2v_{sj}^{ab} - v_{js}^{ab})}{\epsilon_s^+ + \epsilon_j - \epsilon_a - \epsilon_b} + \sum_{ijsb} \frac{v_{ij}^{sb} (2v_{ij}^{sb} - v_{ji}^{sb})}{\epsilon_i + \epsilon_j - \epsilon_s^- - \epsilon_b} \\ + \frac{1}{4} \sum_{stab} \frac{(v_{st}^{ab} - v_{ts}^{ab})(v_{st}^{ab} - v_{ts}^{ab})}{\epsilon_s^+ + \epsilon_t^+ - \epsilon_a - \epsilon_b} + \frac{1}{4} \sum_{ijst} \frac{(v_{ij}^{st} - v_{ji}^{st})(v_{ij}^{st} - v_{ji}^{st})}{\epsilon_i + \epsilon_j - \epsilon_s^- - \epsilon_t^-}, \quad (24)$$

$$E_2^{\text{OPT2}} = \frac{1}{2} \sum_{ia} \frac{K_i^a K_i^a}{\epsilon_i - \epsilon_a} + \sum_{jbs \neq t} \frac{v_{sj}^{bt} v_{sj}^{bt}}{\epsilon_s^+ + \epsilon_j - \epsilon_b - \epsilon_t^-} + \sum_{jbs} \frac{v_{sj}^{bs} v_{sj}^{bs}}{\epsilon_j - \epsilon_b} + \sum_{ijab} \frac{v_{ij}^{ab} (2v_{ij}^{ab} - v_{ji}^{ab})}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} + \sum_{sjab} \frac{v_{sj}^{ab} (2v_{sj}^{ab} - v_{js}^{ab})}{\epsilon_s^+ + \epsilon_j - \epsilon_a - \epsilon_b} \\ + \sum_{ijsb} \frac{v_{ij}^{sb} (2v_{ij}^{sb} - v_{ji}^{sb})}{\epsilon_i + \epsilon_j - \epsilon_s^- - \epsilon_b} + \frac{1}{4} \sum_{stab} \frac{(v_{st}^{ab} - v_{ts}^{ab})(v_{st}^{ab} - v_{ts}^{ab})}{\epsilon_s^+ + \epsilon_t^+ - \epsilon_a - \epsilon_b} + \frac{1}{4} \sum_{ijst} \frac{(v_{ij}^{st} - v_{ji}^{st})(v_{ij}^{st} - v_{ji}^{st})}{\epsilon_i + \epsilon_j - \epsilon_s^- - \epsilon_t^-}, \quad (25)$$

$$E_2^{\text{OPT1}} = \frac{1}{2} \sum_{ia} \frac{K_i^a K_i^a}{\epsilon_i - \epsilon_a} + \sum_{sjbt} \frac{v_{sj}^{bt} v_{sj}^{bt}}{f_s + \epsilon_j - \epsilon_b - f_t} + \sum_{ijab} \frac{v_{ij}^{ab} (2v_{ij}^{ab} - v_{ji}^{ab})}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} + \sum_{sjab} \frac{v_{sj}^{ab} (2v_{sj}^{ab} - v_{js}^{ab})}{f_s + \epsilon_j - \epsilon_a - \epsilon_b} + \sum_{ijsb} \frac{v_{ij}^{sb} (2v_{ij}^{sb} - v_{ji}^{sb})}{\epsilon_i + \epsilon_j - f_s - \epsilon_b} \\ + \frac{1}{4} \sum_{stab} \frac{(v_{st}^{ab} - v_{ts}^{ab})(v_{st}^{ab} - v_{ts}^{ab})}{f_s + f_t - \epsilon_a - \epsilon_b} + \frac{1}{4} \sum_{ijst} \frac{(v_{ij}^{st} - v_{ji}^{st})(v_{ij}^{st} - v_{ji}^{st})}{\epsilon_i + \epsilon_j - f_s - f_t}, \quad (26)$$

where

$$K_i^a = - \sum_s v_{ia}^{ss}, \quad (27)$$

Close examination of Eqs. (24)–(26) shows that at second-order the computational cost of OPT1, OPT2, and ZAPT is essentially identical, and that the only difference between these theories involves the denominators. In particular, the difference between ZAPT and OPT2 is very minor—only involving the second term in Eq. (24) and the third term in Eq. (25) (note that the second term in ZAPT is split into two terms for OPT2, where certain of the semidiagonal elements are treated differently). As it turns out, this minor difference leads to a rather undesirable feature in the OPT2 formula-

tion. For example, consider a high-spin triplet electronic state in which the two singly occupied orbitals are different components of a degenerate molecular orbital, such as the twisted D_{2d} form of triplet C_2H_4 where the two CH_2 groups lie in perpendicular planes or the $X^3\Sigma_g^-$ state of O_2 . Examination of the second and third terms of Eq. (25) shows that when $s \neq t$ the contribution to the second-order energy is different than if $s = t$ even though s and t are simply different components of a degenerate molecular orbital. This leads to E_2^{OPT2} being noninvariant with respect to orbital mixings between s and t . For example, for D_{2d} triplet C_2H_4 we obtain either $-0.221\,286$ or $-0.222\,672$ simply by running the calculation in the D_2 or C_{2v} subgroups, respectively (performed at the geometry reported in Ref. 5, using the 6-31G* basis

set). In C_1 symmetry or when the degenerate orbitals are within the same irreducible representation, we are free to apply an arbitrary rotation to the components of the degenerate orbital, while still maintaining canonical orbitals. Thus for C_2H_4 we happen to obtain an energy of $-0.221\,386$, although this can be arbitrarily changed, within limits. We have shown through explicit calculation that none of the other methods investigated here exhibit this problem. Another example is given by evaluating E_2^{OPT2} for $X^3\Sigma_g^- O_2$ using either D_{2h} ($-0.371\,29$) or $D_{\infty h}$ ($-0.370\,53$) symmetry at $r=1.239\text{ \AA}$, in a standard DZP basis set. Clearly this is an undesirable feature, especially when computing vibrational frequencies about the symmetric point for molecules that have nontotally symmetric vibrations, such as $D_{2d} C_2H_4$, since this shows that OPT2 energies are not differentiable in this situation.

In the quest for a perturbation theory applicable to the relativistic Dirac-Fock equations, Dyall²⁵ has recently proposed a modification in the definition of the OPT2 H_0 in which degenerate open-shell orbitals will be treated consistently thereby eliminating this noninvariance. However, the modified theory moves closer to OPT1 (and further away from ZAPT) suggesting that the perturbation series will not converge as well as OPT2 or ZAPT. The interested reader is referred to Ref. 25 for a more detailed account of this modified OPT2 approach.

As indicated above, the computational cost of OPT1, OPT2, and ZAPT is the same at second-order, but more importantly, this cost is essentially the same as that for an analogous closed-shell system. For all three methods, the main cost will arise from the "closed-shell" term, the third term in Eqs. (24) and (26) and the fourth term in Eq. (25), and this term is identical in form and cost to the closed-shell MP2 energy. Thus, unlike RMP and ROMP, the OPT1, OPT2, and ZAPT methods all require similar cost to closed-shell MP theory at second-order. Given the nature of the first-order wave functions, it is straightforward to show that this similarity in cost will carry over to the third-order energies as well (examination of the MP third-order energy expression²⁶ helps to clarify this point). At fourth order, it has been pointed out by Murray and Handy¹⁵ that because of the nature of the OPT2 H_0 , the factorization of the contribution from quadruple excitations that reduces the cost from order N^8 to order N^6 (where N is the number of molecular orbitals) is not possible. However, this lack of factorization only applies to a small number of terms where an open-shell orbital has a dual function as both occupied and virtual. Thus the cost of OPT2 at fourth order will not be much greater than that of ZAPT.

Given the similarity of H_0 for OPT1 and ZAPT (mentioned earlier), it is reasonable to conclude that the computational cost of OPT1 will either be similar to that of ZAPT at all orders or less than that of ZAPT. In order to evaluate the cost for ZAPT at higher orders (higher than third), it is useful to consider the discussion of the symmetry properties of wave functions constructed from symmetric spin orbitals presented in Ref. 20. From this discussion it is apparent that when an excitation level appears for the first time in an n th-order wave function, the symmetry relationship for the

"closed-shell" amplitudes (i.e., those amplitudes that are indexed only by doubly occupied and unoccupied orbitals in the reference function—these make up the majority of the amplitudes) that multiply determinants from this excitation level will be identical to those in standard closed-shell MP theory. Because the limiting step in computational cost for a given E_n will always arise from an excitation level first appearing in the $(n-1)/2$ -order wave function for n odd, and $n/2$ -order wave function for n even, it is clear that the limiting computational cost for ZAPT will always be the same as that for closed-shell MP theory. However, it is also apparent from the discussion in Ref. 20 that because the relationships among the "closed-shell" amplitudes become more complicated in subsequent perturbed wave functions, the lower-order computational cost will increase. For example, for fourth-order the N^7 cost of ZAPT will be the same as for closed-shell fourth-order MP theory, but the number of N^6 steps will be larger for ZAPT than for closed-shell theory. The arguments presented herein may be easily verified by examination of the spin-orbital equations²⁷ for the N^7 steps in fourth-order MP theory.

No mention has yet been made of the so-called "direct" perturbation theory implementations.^{28,29} These are methods in which atomic orbital integrals are computed as they are needed, and are not stored on disk. In terms of computational cost, the OPT1, OPT2, and ZAPT methods have an obvious advantage over the RMP and ROMP methods as the former have only one set of spatial molecular orbitals whereas the latter have two sets. Moreover, for the very same reasons, the application of analytical gradient theory to OPT1, OPT2, and ZAPT will be much simpler and will lead to much more efficient formula than for RMP and ROMP.

In summary, at low orders of perturbation theory (second and third) the RHF open-shell perturbation theories discussed here will increase in computational effort in the order $OPT1=OPT2=ZAPT < RMP=ROMP$, and OPT1, OPT2, and ZAPT will exhibit computational cost similar to closed-shell MP theory. At fourth-order, the order of increasing cost will be closed-shell MP theory $\approx OPT1 \approx ZAPT \approx OPT2 < RMP=ROMP$. Based on the symmetry properties of wave functions constructed from symmetric spin orbitals, it has been argued that the limiting computational step for ZAPT will always be similar in cost to that for closed-shell MP theory, but that the computational effort in lower order steps will be larger for ZAPT relative to closed-shell MP theory.

IV. NUMERICAL COMPARISONS

As a first comparison of the various RHF open-shell perturbation theories, we have examined the equilibrium structures and harmonic vibrational frequencies of $X^3\Sigma_g^- O_2$, $a^3\Pi_u C_2$, $X^2\Sigma^+ CN$, $X^2\Pi NO$, $X^3B_1 CH_2$, $X^2B_1 NH_2$, $X^2A_1 BH_2$, $X^2B_1 H_2O^+$, $X^2A'' HNF$, and $X^2A_1 NO_2$, using both the triple zeta with two sets of polarization functions (TZ2P) and TZ2P plus an additional f function on the heavy atoms and a d function on H (TZ2Pf) basis sets. The TZ2P basis sets are Dunning's³⁰ ($5s4p/3s$) contractions of Huzinaga's³¹ ($10s6p/5s$) primitive sets. All of the polarization function orbital exponents are contained in Ref. 32. In all calculations, the heavy atom core $1s$ -like molecular orbit-

TABLE I. Comparison of second-order perturbation theory energies (E_h), equilibrium geometries, and vibrational frequencies (cm^{-1}) for O_2 , C_2 , CN, and NO.^a

	ZAPT	OPT1	OPT2	RMP	ROMP	Expt. ^b
$\text{O}_2/\text{TZ2P}$						
E^c	0.099 056	0.147 149	0.105 476	0.105 310	0.110 494	...
r	1.2476	1.3551	1.2521	1.2618	1.2668	1.2075
ω	1304.4	606.8	1283.9	1200.1	1168.5	1580.2
$\text{O}_2/\text{TZ2Pf}$						
E^c	0.139 857	0.186 394	0.146 244	0.145 914	0.150 986	...
r	1.2376	1.3192	1.2418	1.2499	1.2542	1.2075
ω	1368.9	807.6	1348.7	1273.3	1244.4	1580.2
$\text{C}_2/\text{TZ2P}$						
E^d	0.734 180	0.763 275	0.737 640	0.739 923	0.741 911	...
r	1.3169	1.3260	1.3182	1.3198	1.3199	1.3119
ω	1640.8	1598.8	1634.2	1626.6	1627.9	1641.4
$\text{C}_2/\text{TZ2Pf}$						
E^d	0.753 186	0.782 656	0.756 695	0.758 947	0.760 963	...
r	1.3164	1.3254	1.3177	1.3192	1.3193	1.3119
ω	1650.3	1609.1	1643.7	1636.4	1637.7	1641.4
$\text{CN}/\text{TZ2P}$						
E^e	0.524 994	0.535 513	0.526 934	0.527 170	0.526 073	...
r	1.1871	1.1980	1.1880	1.1902	1.1886	1.1718
ω	1854.5	1732.0	1844.5	1816.8	1832.7	2068.6
$\text{CN}/\text{TZ2Pf}$						
E^e	0.548 818	0.559 547	0.550 772	0.551 026	0.549 914	...
r	1.1878	1.1989	1.1887	1.1910	1.1893	1.1718
ω	1853.7	1729.1	1843.3	1815.7	1831.1	2068.6
$\text{NO}/\text{TZ2P}$						
E^f	0.676 150	0.689 559	0.678 214	0.677 479	0.678 571	...
r	1.1579	1.1638	1.1585	1.1597	1.1585	1.1508
ω	1895.8	1866.3	1895.6	1882.3	1899.9	1904.2
$\text{NO}/\text{TZ2Pf}$						
E^f	0.711 902	0.725 404	0.713 980	0.713 253	0.714 333	...
r	1.1559	1.1616	1.1565	1.1577	1.1564	1.1508
ω	1923.6	1894.4	1923.2	1910.1	1927.5	1904.2

^aBond lengths in Å. Electronic states are $X^3\Sigma^-$, $a^3\Pi_u$, $X^2\Sigma^+$, and $X^2\Pi$ for O_2 , C_2 , CN, and NO, respectively.

^bReference 35.

^cThe energy is reported as $-(E+150)$.

^dThe energy is reported as $-(E+75)$.

^eThe energy is reported as $-(E+92)$.

^fThe energy is reported as $-(E+129)$.

als were frozen, and six-component d functions and ten-component f functions were used. In the presentation of the theoretical geometries and harmonic frequencies, more decimal places are included than is normally considered relevant in order to distinguish between the various perturbation theories for those systems that display only small differences. The calculations were performed either with programs developed at Daresbury Laboratory that are interfaced to the SEWARD (Ref. 33) integral program, or with programs developed at NASA Ames Research Center, some of which are interfaced to the MOLECULE-SWEDEN (Ref. 34) program system.

The equilibrium bond distances and harmonic frequencies of the diatomics, obtained with the various methods, are contained in Table I. For comparison, the experimental quantities³⁵ are also included. Examination of Table I shows that the OPT1 method yields the least reliable results, and also gives results that are significantly different from those of the other methods. In particular, r_e for O_2 is 0.15–0.12 Å too long and ω_e is 700–900 cm^{-1} too low. Based on the earlier assertions that the OPT1 perturbation series displays erratic behavior,¹⁵ it is not too surprising that OPT1 yields the poorest results.

The agreement among the other methods for the bond distances and frequencies is generally good, with the only exception being O_2 . For O_2 , the OPT2 and ZAPT methods show markedly better performance than the RMP and ROMP methods, although the difference between experiment and the OPT2 and ZAPT results is still rather large. It has been shown previously that second-order perturbation theory does not perform well for ground state O_2 , but in many instances this type of molecule is useful to better elucidate the differences between perturbation theory methods that are similar. In other words, a "difficult molecule" such as O_2 magnifies the differences between the various methods, and gives a better indication of how easily each method breaks down. The agreement between experiment and the ZAPT, OPT2, RMP, and ROMP methods for C_2 and NO is quite good. For CN, the agreement is generally much better than for O_2 . The only exception is for the harmonic frequency (with the TZ2Pf basis set) where the error for both molecules is about 200–300 cm^{-1} .

The equilibrium structures and harmonic vibrational frequencies for CH_2 , NH_2 , BH_2 , H_2O^+ , HNF , and NO_2 are presented in Tables II–VII, respectively. Examination of these again shows that the OPT1 equilibrium geometries and

TABLE II. Comparison of second-order perturbation theory energies (E_h), equilibrium geometries, and vibrational frequencies (cm^{-1}) for $X^3B_1\text{CH}_2$.^a

	ZAPT	OPT1	OPT2	RMP	ROMP	Expt. ^b
TZ2P						
E	0.045 431	0.054 979	0.047 228	0.047 494	0.047 192	...
r_{CH}	1.0723	1.0741	1.0726	1.0732	1.072 5	1.0750
$\angle\text{HCH}$	132.57	133.10	132.98	132.41	132.81	133.88
$\omega_1(a_1)$	3211.9	3190.9	3208.7	3201.7	3 208.9	3020.7
$\omega_2(a_1)$	1164.9	1141.7	1148.3	1168.2	1 156.3	963.1
$\omega_3(b_2)$	3444.3	3426.5	3443.0	3434.3	3 443.4	3152.5
TZ2Pf						
E	0.056 313	0.066 156	0.058 132	0.058 436	0.058 108	...
r_{CH}	1.0731	1.0749	1.0733	1.0739	1.0734	1.0750
$\angle\text{HCH}$	132.99	133.60	133.44	132.83	133.24	133.88
$\omega_1(a_1)$	3212.0	3191.4	3209.1	3201.9	3208.9	3020.7
$\omega_2(a_1)$	1137.2	1110.5	1118.9	1140.6	1127.7	963.1
$\omega_3(b_2)$	3446.2	3429.2	3445.4	3436.5	3445.3	3152.5

^aBond lengths in Å and angles in degrees. The energy is reported as $-(E + 39)$.

^bExperimental equilibrium geometry and fundamental frequencies from Ref. 44.

harmonic frequencies deviate most from the other perturbation theories, although the differences between all of the methods are fairly small for this set of molecules, especially for the dihydrides. The results for the NO_2 molecule display the largest differences, but even here the maximum differences between the ZAPT, OPT2, RMP, and ROMP methods is only 0.0021 Å, 0.36°, and 17.1 cm^{-1} . Based on this set of triatomics, it is evident that there is not much to choose between the various perturbation theories.

The agreement between theory and experiment is generally good for this set of molecules, especially taking into account that most of the experimental results refer to vibrationally averaged structures and fundamental frequencies. It should be noted that it is typical for the anharmonic correction to the bending modes of dihydrides to be reasonably large (e.g., see Refs. 36,37). In addition, the anharmonic cor-

TABLE III. Comparison of second-order perturbation theory energies (E_h), equilibrium geometries, and vibrational frequencies (cm^{-1}) for $X^2B_1\text{NH}_2$.^a

	ZAPT	OPT1	OPT2	RMP	ROMP	Expt. ^b
TZ2P						
E	0.758 821	0.765 216	0.760 189	0.759 629	0.759 905	...
r_{NH}	1.0207	1.0219	1.0210	1.0209	1.0209	1.024
$\angle\text{HNNH}$	103.07	103.00	103.07	103.07	103.07	103.3
$\omega_1(a_1)$	3453.3	3440.8	3450.7	3451.7	3451.9	3219.4
$\omega_2(a_1)$	1562.9	1558.8	1562.4	1562.4	1562.4	1497.3
$\omega_3(b_2)$	3555.8	3543.4	3553.0	3554.2	3554.4	3301.1
TZ2Pf						
E	0.776 395	0.783 044	0.777 809	0.777 230	0.777 501	...
r_{NH}	1.0214	1.0225	1.0216	1.0215	1.0215	1.024
$\angle\text{HNNH}$	103.01	102.94	103.00	102.99	103.00	103.3
$\omega_1(a_1)$	3450.1	3437.9	3447.4	3448.4	3448.7	3219.4
$\omega_2(a_1)$	1550.6	1546.7	1550.1	1550.2	1550.1	1497.3
$\omega_3(b_2)$	3557.4	3545.3	3554.5	3555.6	3556.0	3301.1

^aBond lengths in Å and angles in degrees. The energy is reported as $-(E + 55)$.

^bVibrationally averaged geometry from Ref. 45 and fundamental frequencies from Ref. 46.

TABLE IV. Comparison of second-order perturbation theory energies (E_h), equilibrium geometries, and vibrational frequencies (cm^{-1}) for $X^2A_1\text{BH}_2$.^a

	ZAPT	OPT1	OPT2	RMP	ROMP	Expt. ^b
TZ2P						
E	0.836 394	0.839 213	0.836 861	0.836 922	0.836 772	...
r_{BH}	1.1834	1.1842	1.1834	1.1837	1.1834	1.181
$\angle\text{HBH}$	128.34	128.51	128.51	128.31	128.39	131
$\omega_1(a_1)$	2639.5	2631.8	2639.0	2636.1	2638.7	
$\omega_2(a_1)$	1057.5	1048.4	1050.1	1057.1	1055.4	
$\omega_3(b_2)$	2802.2	2795.7	2802.5	2799.1	2801.8	
TZ2Pf						
E	0.843 872	0.846 781	0.844 346	0.844 409	0.844 251	...
r_{BH}	1.1836	1.1844	1.1837	1.1840	1.1837	1.181
$\angle\text{HBH}$	128.61	128.82	128.78	128.57	128.65	131
$\omega_1(a_1)$	2645.6	2638.2	2644.9	2641.9	2644.6	
$\omega_2(a_1)$	1042.0	1031.6	1034.3	1041.8	1040.0	
$\omega_3(b_2)$	2809.7	2803.8	2809.8	2806.4	2809.1	

^aBond lengths in Å and angles in degrees. The energy is reported as $-(E + 25)$.

^bVibrationally averaged structure from Ref. 47.

rection for the bending mode in $^3B_1\text{CH}_2$ is probably even larger than normal owing to the very flat bending potential for this molecule. The experimental data available for NO_2 include harmonic frequencies, and for this system the agreement between theory and experiment for ω_1 and ω_2 is reasonably good. The agreement for the antisymmetric N–O stretch ω_3 , however, is not very good, with the *ab initio* results being consistently about 150 cm^{-1} too high. This type of behavior for second-order perturbation theory has been noted previously^{38–40} for the closed-shell species HONO_2 , CH_3ONO_2 , and ClONO_2 , and so is not limited to the open-shell system NO_2 , but seems to be a feature of the NO_2 moiety.

Examination of the second-order energies in Tables I–VII shows that in every case the OPT1 method yields the lowest energy, and that the ZAPT method gives the highest

TABLE V. Comparison of second-order perturbation theory energies (E_h), equilibrium geometries, and vibrational frequencies (cm^{-1}) for $X^2B_1\text{H}_2\text{O}^+$.^a

	ZAPT	OPT1	OPT2	RMP	ROMP	Expt. ^b
TZ2P						
E	0.843 602	0.850 049	0.845 112	0.844 452	0.844 664	...
r_{OH}	0.9968	0.9979	0.9970	0.9970	0.9970	0.999
$\angle\text{HOH}$	109.10	109.04	109.12	109.09	109.09	110.5
$\omega_1(a_1)$	3430.5	3418.8	3428.7	3429.2	3428.9	3213.0
$\omega_2(a_1)$	1490.1	1487.1	1489.4	1489.9	1489.7	1408.4
$\omega_3(b_2)$	3489.7	3478.3	3487.8	3488.4	3488.1	3259.0
TZ2Pf						
E	0.863 862	0.870 594	0.865 430	0.864 749	0.864 949	...
r_{OH}	0.9978	0.9988	0.9979	0.9979	0.9979	0.999
$\angle\text{HOH}$	109.33	109.27	109.35	109.32	109.32	110.5
$\omega_1(a_1)$	3427.1	3415.8	3425.2	3425.8	3425.6	3213.0
$\omega_2(a_1)$	1472.5	1469.5	1471.7	1472.3	1472.1	1408.4
$\omega_3(b_2)$	3488.8	3477.6	3486.8	3487.5	3487.3	3259.0

^aBond lengths in Å and angles in degrees. The energy is reported as $-(E + 75)$.

^bVibrationally averaged structure from Ref. 47 and fundamental frequencies from Ref. 48.

TABLE VI. Comparison of second-order perturbation theory energies (E_h), equilibrium geometries, and vibrational frequencies (cm^{-1}) for X^2A'' HNF.^a

	ZAPT	OPT1	OPT2	RMP	ROMP	Expt. ^b
TZ2P						
E	0.819 922	0.828 485	0.821 658	0.821 256	0.821 045	...
r_{HN}	1.0256	1.0269	1.0259	1.0258	1.0258	(1.06)
r_{NF}	1.3732	1.3715	1.3730	1.3739	1.3729	1.37
$\angle \text{HNF}$	100.00	100.00	100.00	99.96	99.99	105
$\omega_1(a')$	3414.0	3398.6	3411.0	3412.3	3412.5	3167
$\omega_2(a')$	1038.0	1046.8	1038.7	1038.6	1038.2	1015
$\omega_3(a')$	1483.9	1482.6	1483.4	1483.0	1483.9	1439
TZ2Pf						
E	0.861 095	0.869 909	0.862 866	0.862 452	0.862 247	...
r_{HN}	1.0268	1.0281	1.0271	1.0269	1.0270	(1.06)
r_{NF}	1.3622	1.3608	1.3621	1.3628	1.3619	1.37
$\angle \text{HNF}$	100.23	100.24	100.24	100.20	100.25	105
$\omega_1(a')$	3405.9	3391.1	3403.2	3404.7	3404.7	3167
$\omega_2(a')$	1066.9	1075.6	1067.7	1067.7	1067.6	1015
$\omega_3(a')$	1483.9	1482.5	1483.4	1483.1	1484.0	1439

^aBond lengths in Å and angles in degrees. The energy is reported as $-(E + 154)$. The HNF bend is given by ω_2 .

^bVibrationally averaged structure from Ref. 47 (the NH bond distance was assumed) and fundamental frequencies from Ref. 49.

energy. The fact that the OPT1 method yields the lowest energy is consistent with earlier studies,^{14,15} which assert that the OPT1 perturbation series does not converge very rapidly, and that this is due to "small denominators" leading to a larger (in magnitude) second-order energy. Moreover, the conclusions of studies in which the convergence of perturbation series was investigated would suggest that the ZAPT series should display the most rapid convergence of the open-shell perturbation theories studied here because its smallest (in magnitude) second-order energy suggests that it possesses the "largest denominators."

Finally, in Table VIII the singlet-triplet energy differences for CH_2 and SiH_2 are presented and compared with full configuration interaction (FCI) values.^{41,42} Before discussing the results, it is important to consider a few points. It is generally accepted that due to the Fermi-hole concept,⁴³ the self-consistent-field (SCF) level of theory tends to provide a better description of high-spin states relative to low-spin states. In other words, in the present example there is generally more electron correlation present in the singlet states relative to the triplet states. Therefore, since the ZAPT method usually gives the smallest (in magnitude) second-order energy and the OPT1 method generally gives the largest, it may be expected that the ZAPT method will yield

TABLE VII. Comparison of second-order perturbation theory energies (E_h), equilibrium geometries, and vibrational frequencies (cm^{-1}) for X^2A_1 NO_2 .^a

	ZAPT	OPT1	OPT2	RMP	ROMP	Expt. ^b
TZ2P						
E	0.747 997	0.767 267	0.750 448	0.750 333	0.751 396	...
r_{NO}	1.2075	1.2159	1.2087	1.2090	1.2095	1.1946
$\angle \text{ONO}$	132.58	131.72	132.40	132.59	132.23	133.85
$\omega_1(a_1)$	1308.5	1266.9	1300.9	1302.3	1295.8	1348.8
$\omega_2(a_1)$	769.5	758.7	768.3	766.5	767.6	759.5
$\omega_3(b_2)$	1801.0	1785.6	1783.9	1797.2	1792.2	1671.4
TZ2Pf						
E	0.807 514	0.826 652	0.809 935	0.809 835	0.810 867	...
r_{NO}	1.2037	1.2116	1.2048	1.2051	1.2056	1.1946
$\angle \text{ONO}$	132.86	132.04	132.70	132.89	132.53	133.85
$\omega_1(a_1)$	1331.0	1290.9	1324.0	1325.0	1319.1	1348.8
$\omega_2(a_1)$	768.2	757.4	766.9	765.2	766.3	759.5
$\omega_3(b_2)$	1838.9	1822.7	1823.0	1835.0	1830.6	1671.4

^aBond lengths in Å and angles in degrees. The energy is reported as $-(E + 204)$.

^bEquilibrium geometry from Ref. 50 and harmonic vibrational frequencies from Ref. 51.

singlet-triplet splittings that are closest to the FCI value while the OPT1 method will yield the worst agreement. It should be emphasized that an implicit assumption in this assertion is that the open- and closed-shell perturbation theories will recover about the same percentage of the total correlation energy at second-order. Examination of the results in Table VIII shows that in fact these expectations are correct. The OPT1 singlet-triplet energy differences are always furthest from the FCI results, while the ZAPT results are always in closest agreement. However, it should be noted that at the equilibrium geometries the differences between ZAPT and the OPT2, RMP, and ROMP methods is much smaller than the difference with respect to the FCI method. Thus, while the ZAPT method should generally perform better in determining energy separations between electronic states of differing spin, the overall error will often be much larger than the differences between the ZAPT, OPT2, RMP, and ROMP methods.

V. CONCLUSIONS

Various single-reference perturbation theories based on a RHF reference function have been investigated and contrasted. These include the OPT1, OPT2, RMP (also known as ROHF-MBPT), ROMP, and ZAPT methods. The spin contamination present in the RMP, ROMP, and ZAPT n th-order

TABLE VIII. Comparison of second-order perturbation theory and FCI singlet-triplet splittings for CH_2 and SiH_2 (kcal/mol).

	SCF	OPT1	OPT2	RMP	ROMP	ZAPT	FCI ^a
$\text{CH}_2(\Delta^3B_1 - ^1A_1)$							
r_e	26.136	21.920	17.989	18.048	17.931	17.072	11.971
$\text{SiH}_2(\Delta^1A_1 - ^3B_1)$							
1.0^*r_e	5.488	11.462	14.332	14.146	14.363	15.022	18.343
1.5^*r_e	9.885	9.402	13.619	14.495	14.776	16.255	17.572
2.0^*r_e	-19.068	-19.979	-16.573	-8.292	-9.009	-5.232	4.310

^aFrom Ref. 41 for CH_2 and Ref. 42 for SiH_2 . See these references for details of the calculations.

wave functions has been explicitly shown to result from the fact that S^2 does not commute with H_0 and it has also been shown that there are many more terms in the H_0 for RMP and ROMP that do not commute with S^2 than in the H_0 for ZAPT. The computational costs of the various methods have been discussed, and it is shown that the cost increases according to $\text{OPT1} \approx \text{OPT2} \approx \text{ZAPT} < \text{RMP} = \text{ROMP}$, and that the cost for the OPT1, OPT2, and ZAPT methods is similar to closed-shell MP theory. Furthermore, based on the symmetry properties of wave functions constructed from symmetric spin orbitals, it has been argued that the limiting computational step for ZAPT will be similar in cost to that for closed-shell MP theory, but that the computational effort in less expensive steps (i.e., not limiting steps) will be larger for ZAPT relative to closed-shell MP theory. It is also noted that due to the adoption of only one set of spatial molecular orbitals, the OPT1, OPT2, and ZAPT methods have a major computational advantage over the RMP and ROMP methods for the implementation of so-called “direct” schemes and the application of analytical gradient theory. Examination of the second-order energy expression for OPT2 has revealed that OPT2 has the undesirable property of not being invariant to orbital mixings between open-shell components of a degenerate molecular orbital. Two explicit examples of the magnitude of this noninvariance have been presented.

Finally, equilibrium geometries and harmonic vibrational frequencies of several diatomics and triatomics have been determined at second-order, and these results have shown that in general the OPT1 method yields the least reliable values while the differences between the other methods is usually small. The agreement between experiment and theory (for the ZAPT, OPT2, RMP, and ROMP methods) is shown to be quite good provided that the molecule is reasonably well described by the single determinant reference function. As electron correlation in the molecule becomes more difficult to describe properly, the RMP and ROMP methods appear to break down more readily than the OPT2 and ZAPT methods, although by this stage it is evident that second-order perturbation theory is not really adequate. Singlet–triplet energy separations for CH_2 and SiH_2 are also presented and compared to FCI values. The ZAPT method yields the best singlet–triplet splittings, and an explanation for this is presented (it is also explained why OPT1 singlet–triplet energy differences will usually be the poorest). However, it is also noted that the differences between ZAPT and FCI are usually much larger than the differences between ZAPT and the OPT2, RMP, and ROMP methods.

Based on all of the considerations contained in this study, it is concluded that the ZAPT approach is probably the method of choice. The difference in results between ZAPT and RMP, ROMP, and OPT2 is usually small, and the results tend to be better for ZAPT (and OPT2) relative to RMP and ROMP when the differences become larger. OPT2 has been shown to have an undesirable feature concerning noninvariance to orbital mixings (for degenerate open-shell orbitals) that does not plague ZAPT. Most importantly, the computational cost of ZAPT is similar to that for closed-shell MP theory, and the application of so-called “direct” procedures

and analytical gradient theory is much simpler for ZAPT than for RMP or ROMP theory.

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